# <Division of Synthetic Chemistry> Organoelement Chemistry

# Division of Synthetic Chemistry
## - Organoelement Chemistry -

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## Scope of Research

Organic chemistry has been developed as that of second-row elements such as carbon, oxygen, and nitrogen so far, while the synthesis and isolation of the heavier congeners of typical organic molecules as stable compounds have been one of "dreams" for organic chemists. Our main research interest is the elucidation of the similarities and differences in structures and reactivity between organic compounds and the corresponding heavier congeners. These studies are interesting and important from the standpoints of not only fundamental chemistry but also opening the way to more extensive application of main group chemistry. Organic synthesis mediated by biocatalysts is also studied.

## Research Activities (Year 2008)

### Publications

Sasamori T, Hironaka K, Sugiyama Y, Takagi N, Nagase S, Hosoi Y, Furukawa Y, Tokitoh N: Synthesis and Reactions of a Stable 1,2-Diaryl-1,2-dibromodisilene: A Precursor for Substituted Disilenes and a 1,2-Diaryldisilyne, *J. Am. Chem. Soc.*, **130**, 13856-13857 (2008).

Sasamori T, Yuasa A, Hosoi Y, Furukawa Y, Tokitoh N: 1,2-Bisferrocenyldisilene: A Multi-step Redox System with an Si=Si Double Bond, *Organometallics*, **27**, 3325-3327 (2008).

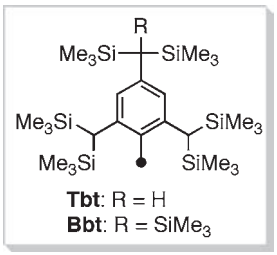
Tanabe T, Mizuhata Y, Takeda N, Tokitoh N: Syntheses and Structures of Platinum Siloxides Bridged by a Sulfur or Selenium Atom and a Unique 1,3-Aryl Migration from Silicon to Platinum through the Si–O–Pt Linkages, *Organometallics*, **27**, 2156-2158 (2008).

### Presentations

Synthesis and Properties of Stable 2-Metallanaphthalenes of Heavier Group 14 Elements, Mizuhata Y, Sasamori T, Nagahora N, Watanabe Y, Furukawa Y, Tokitoh N, Dalton Discussion 11: The Renaissance of Main Group Chemistry, University of California, Berkeley, USA, 24 June 2008 (invited).

Redox Behavior and Coordination Chemistry of Kinetically Stabilized Silaaromatics and Related Compounds, Matsumoto Ta, Tanabe Y, Mizuhata Y, Sasamori S,

## Synthesis of a Novel Silicon–Silicon Triple-Bond Compound




There has been much interest in the chemistry of multiply bonded organosilicon compounds, *i.e.*, disilenes (>Si=Si<) and disilynes (–Si≡Si–). While a lot of kinetically stabilized disilenes have been synthesized and characterized, only two examples of stable disilynes bearing bulky silyl groups have been known up to now. We have reported the synthesis and structure of the first stable 1,2-diaryldisilyne by taking advantage of Bbt groups. The diaryldisilyne has a crystallographic *C*2 axis through the central Si≡Si bond (Figure 1). Its Si≡Si bond length [2.108(5) Å] is reasonably shorter than the typical Si–Si and Si=Si bond lengths, featuring its triple-bond character.

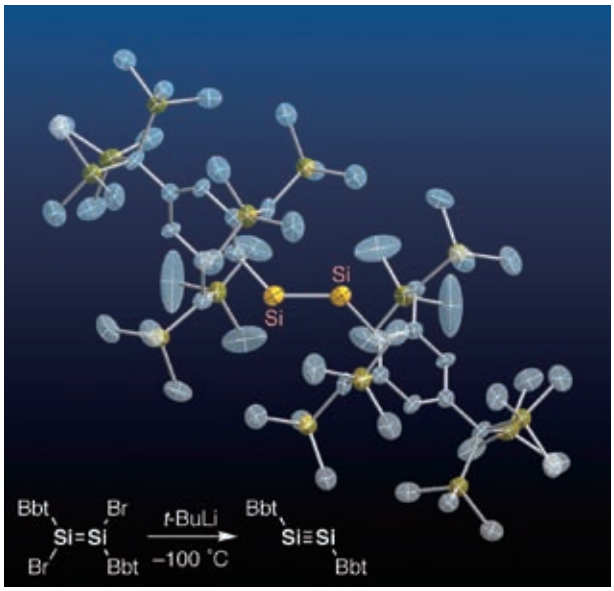



**Figure 1.** Synthesis and Structure of Disilyne (–Si≡Si–).

## 1,3-Aryl Migration from Silicon to Platinum

We have found that platinum siloxides **1** underwent a unique 1,3-migration of the Mes (2,4,6-trimethylphenyl) group from the silicon atom to the platinum center on treatment with chloride ion in the presence of a Brønsted acid, affording the corresponding complexes **2** in moderate yields (Figure 2). It should be noted that the 1,3-migration reactions described here are very important, as they provide the first experimental demonstration of the transmetalation of a carbon substituent from a silicon atom to a transition metal center in a metal siloxide, the process of which is postulated as a plausible mechanism for some silicon-containing catalytic systems, such as the palladium(0) catalyzed cross-coupling reaction of aryl- or alkenylsilanols with aryl or vinyl iodides in the presence of tetrabutylammonium fluoride.

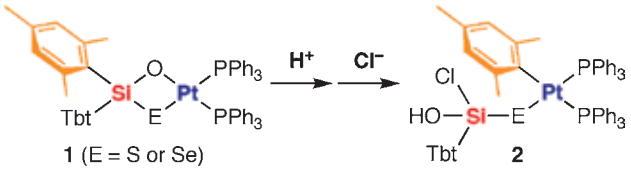



**Figure 2.** 1,3-Mesityl Migration Reaction.

Tokitoh N, The 15th International Symposium on Organosilicon Chemistry, Jeju, Korea, 2 June 2008 (invited).

New Aspects in the Chemistry of Doubly Bonded Systems between Heavier Group 15 Elements, Tokitoh N, Heterocyclic and Heteroatom Chemistry Conference 2008, Cancun, Mexico, 25 Feburary 2008 (invited).

## Grants

Tokitoh N, Sasamori T, Nagahora N, Mizuhata Y, The Chemistry of Unsaturated Compounds of Heavier Main Group Elements: Pursuit of Novel Properties and Functions, Grant-in-Aid for Creative Scientific Research, 1 April 2005–31 March 2010.

Sasamori T, Construction of Novel Extended π-Electron Conjugated Systems Containing Heavier Main Group Elements, Grant-in-Aid for Young Scientists (B), 1 April 2006–31 March 2008.

Sasamori T, Construction of Novel d-π Electron Conjugated Systems Containing Heavier Main Group Elements and Transition Metals and Elucidation of Their Properties. Grant-in-Aid for Science Research on Priority Areas "Synergy of Elements", 1 April 2007–31 March 2010.

Nagahora N, Study on Development of Novel Molecular Devices Bearing Metallocene and Double Bonds between Heavier Group 15 Elements, Kinki Invention Center, 1 April 2007–31 March 2008.

## Awards

Tanabe T, The Best Poster Award, The 2nd Asian Silicon Symposium, 6 June 2008.

Mizuhata Y, Mitsubishi Kagaku Award in Synthetic Organic Chemistry, Japan, 20 February 2008.